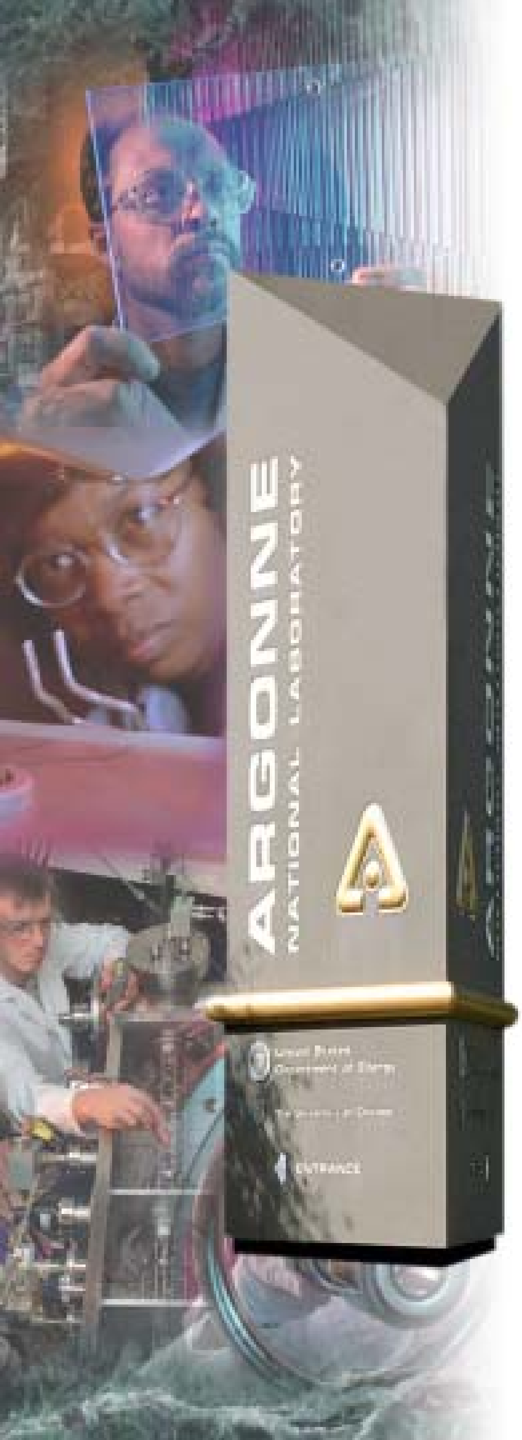


In-situ Pair Distribution Function Analysis: Structural Studies that Probe both Local and Long Range Structure

Peter J. Chupas

Materials Science Division, Argonne National Laboratory

Considerations

What does it take to do in-situ PDF measurements?

High Energy X-rays, Area Detectors

Why PDF?

Catalytic reactions occur on the Å scale.

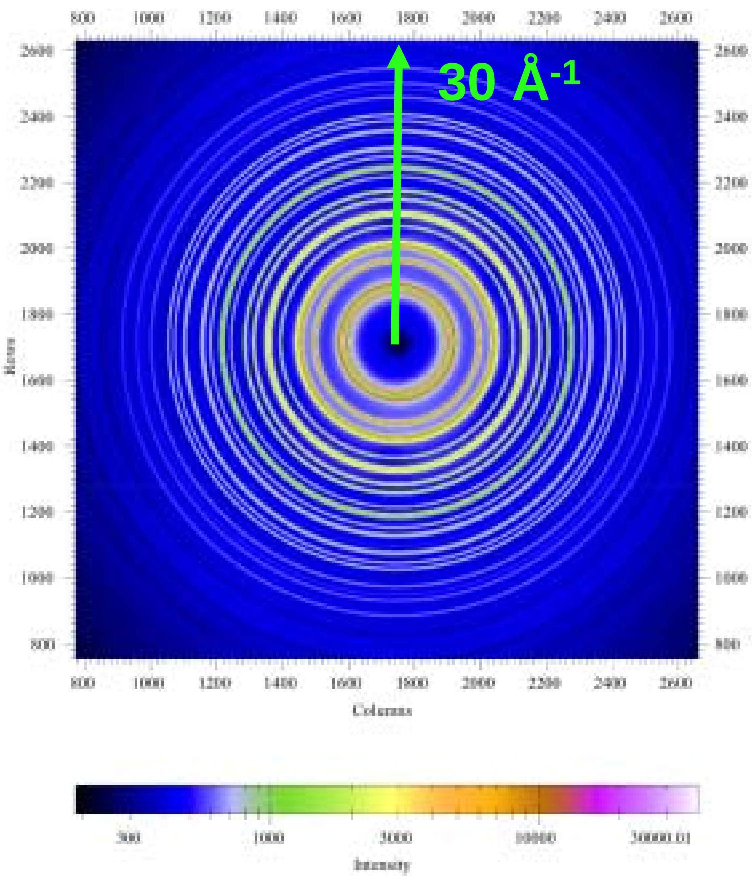
Modeling Structural Data: How can we get more information from our data? As experimentalists should we consult those with expertise in theory and computation?

Applications of in-situ measurements

Phase transitions

Chemical Reactions (Catalysis)

Solid State Reactions



Why use *Area Detectors*?

•With an area detector we can collect all data simultaneously.

•High energy X-rays are a necessity to probe large values of Q over small scattering angles(small detector areas).

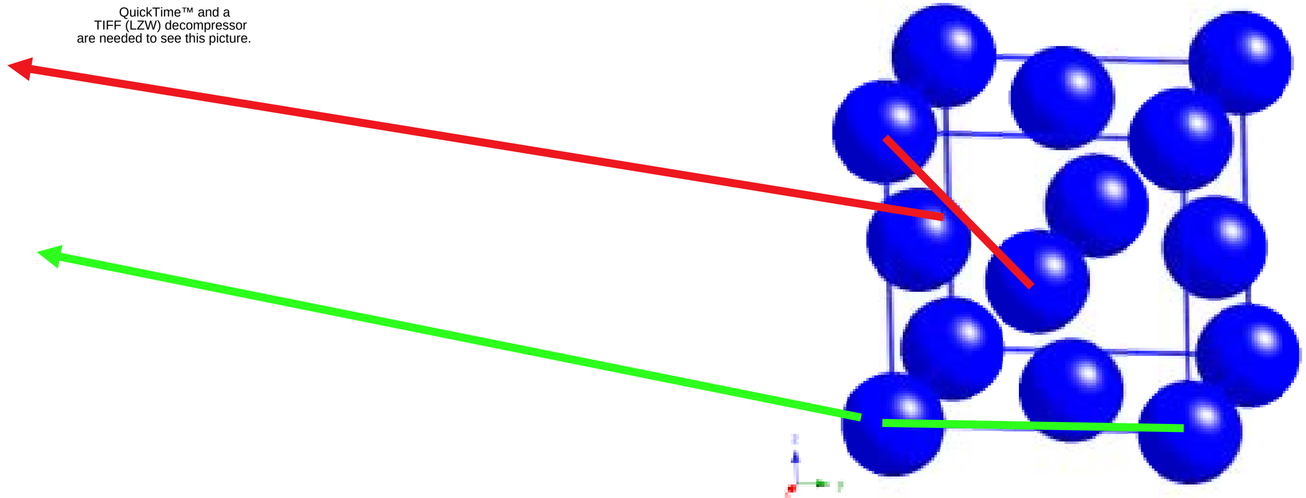
•Counting statistics; averaging over a large solid angle allows adequate statistics for the contribution from Compton scattering to be accurately subtracted.

Chupas, Qiu, Hanson, Lee, Grey, Billinge ***Journal of Applied Crystallography*** **36 (2003) 1342.**

Nickel Collected with an Image Plate

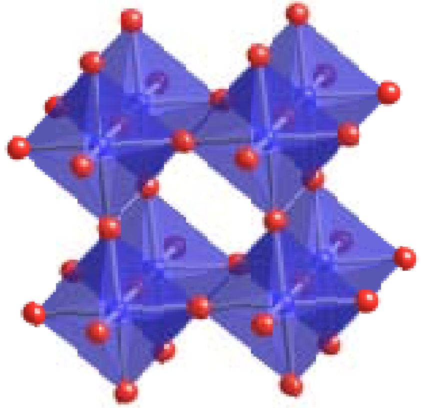
- 1 second counting
- A conventional measurement takes ~8 hours… we need time resolution better than ~1minute for in-situ studies

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

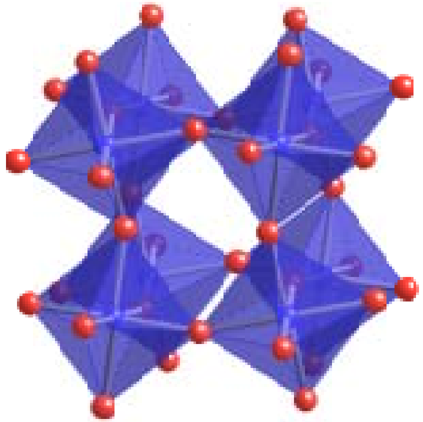


In-situ Powder Diffraction

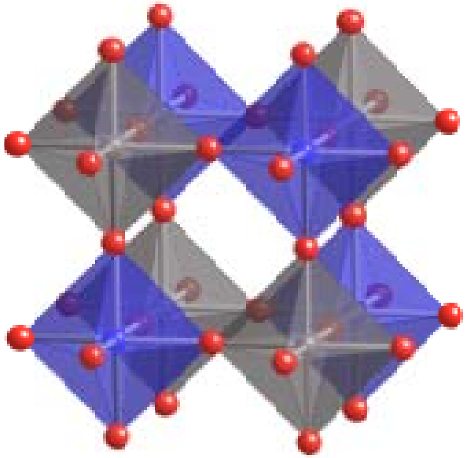
•AlF_3 undergoes a phase transition from a rhombohedrally distorted ReO3 structure to a cubic structure at ~470 C.

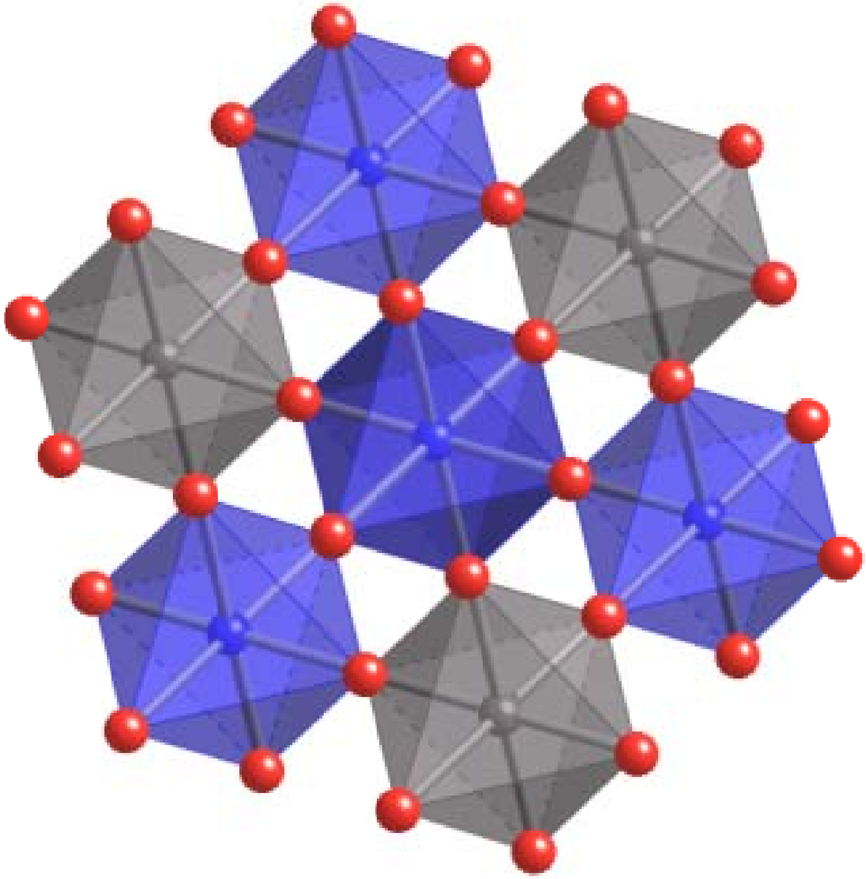


QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.



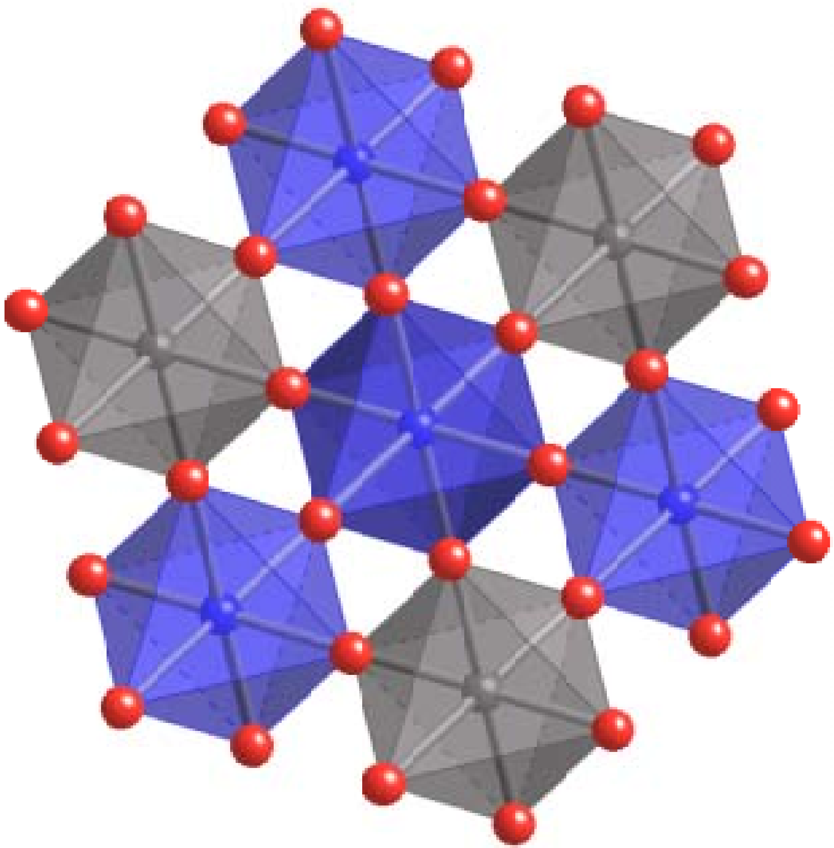
The Structure of α-AlF_3

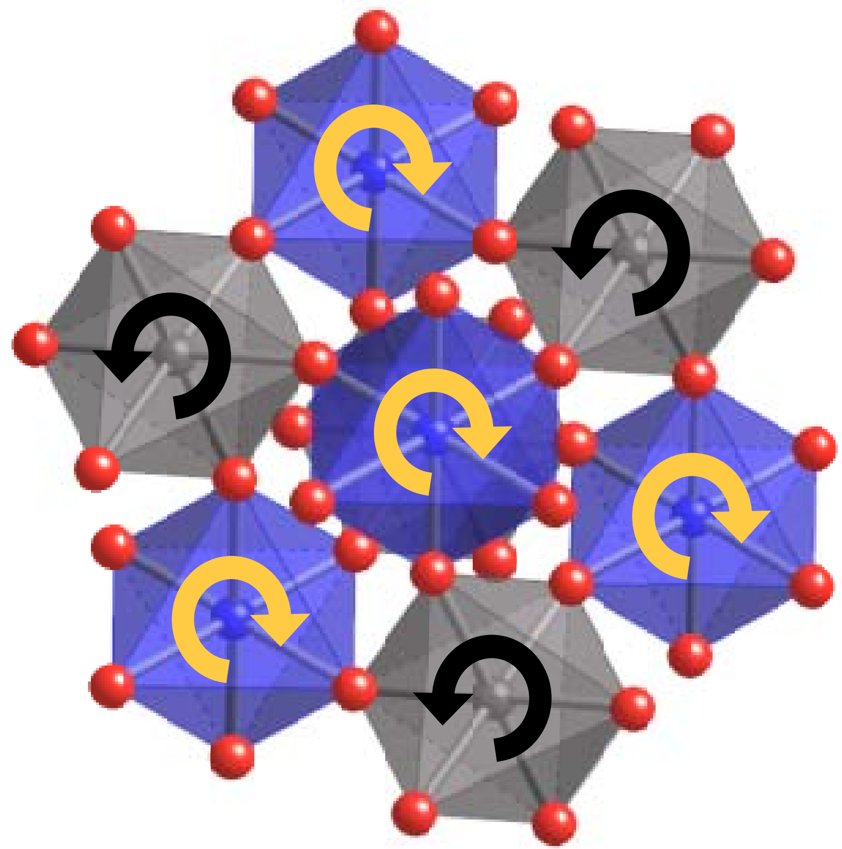




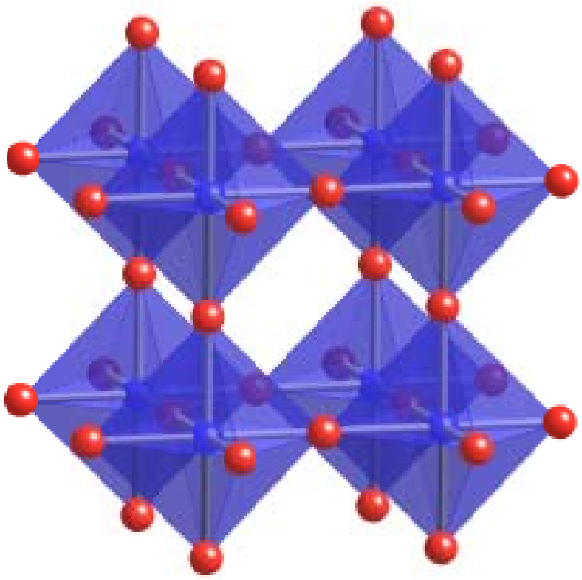
Rotations About the 3-fold Axis

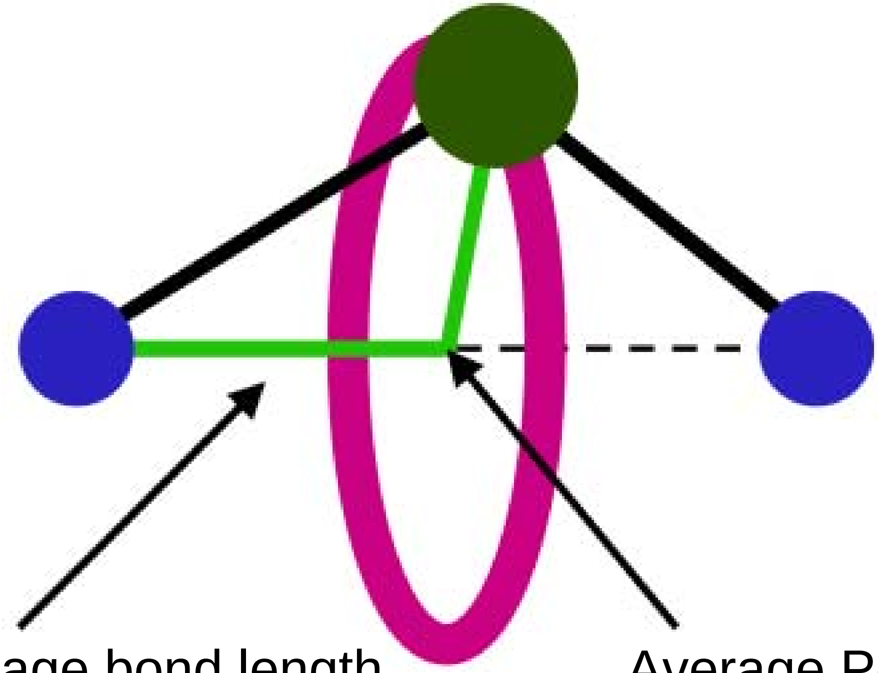
The rhombohedral distortion in α-AlF_3 involves rotations of rigid octahedra





Dynamics in AlF_3 at High Temperature





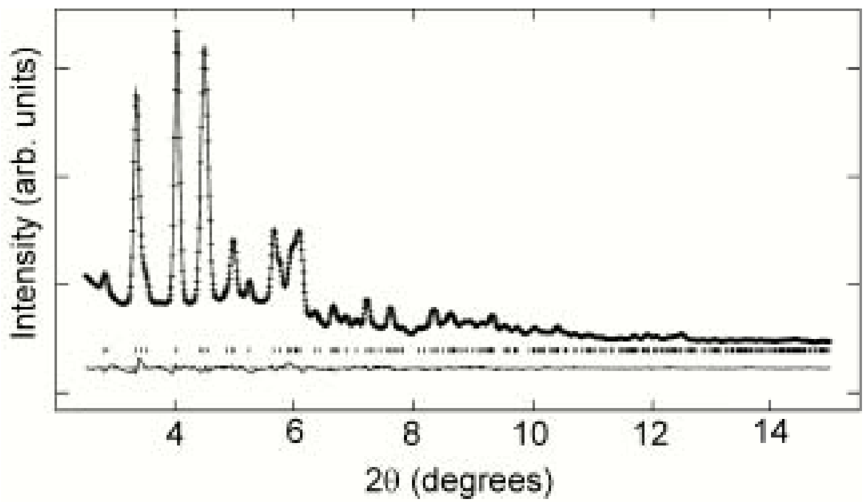
PDF is a measure of the “instantaneous” structure, whereas Rietveld yields the time averaged position of atoms

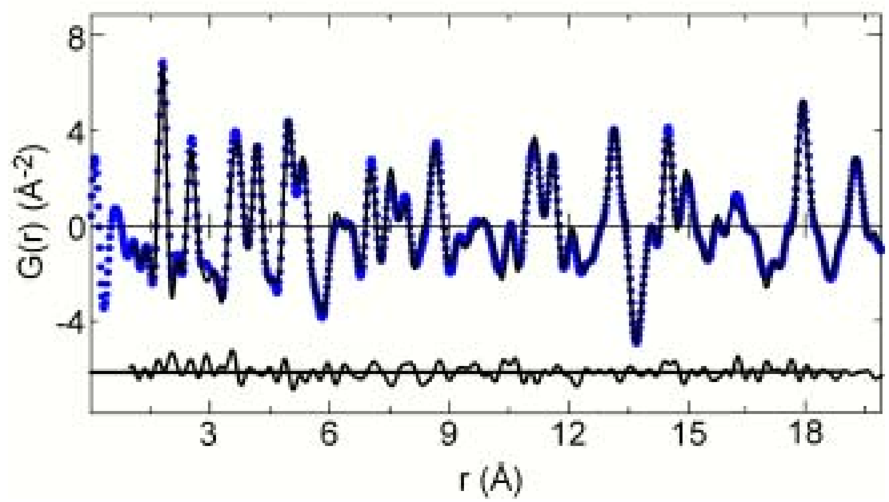
In-situ Pair Distribution Function Analysis

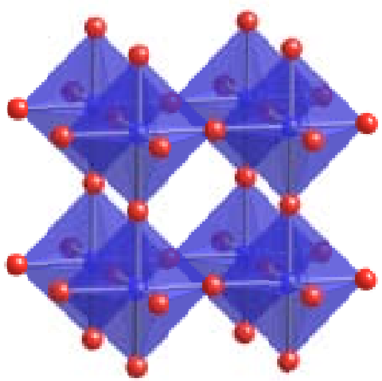
QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Chupas, Chaudhuri, Hanson et al. ***Journal of the American Chemical Society*** **126 (2004) 1342.**

Using a Combination of Analysis Methods

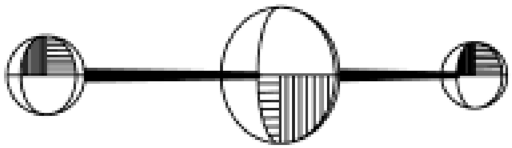






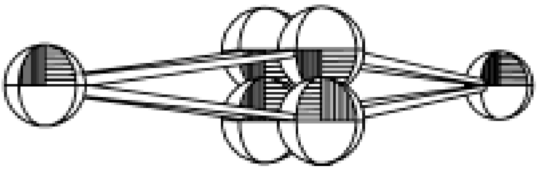
$R_{rietveld}$ = 5.55 %

R_{PDF} = 21.51 %



$R_{rietveld}$ = 5.80 %

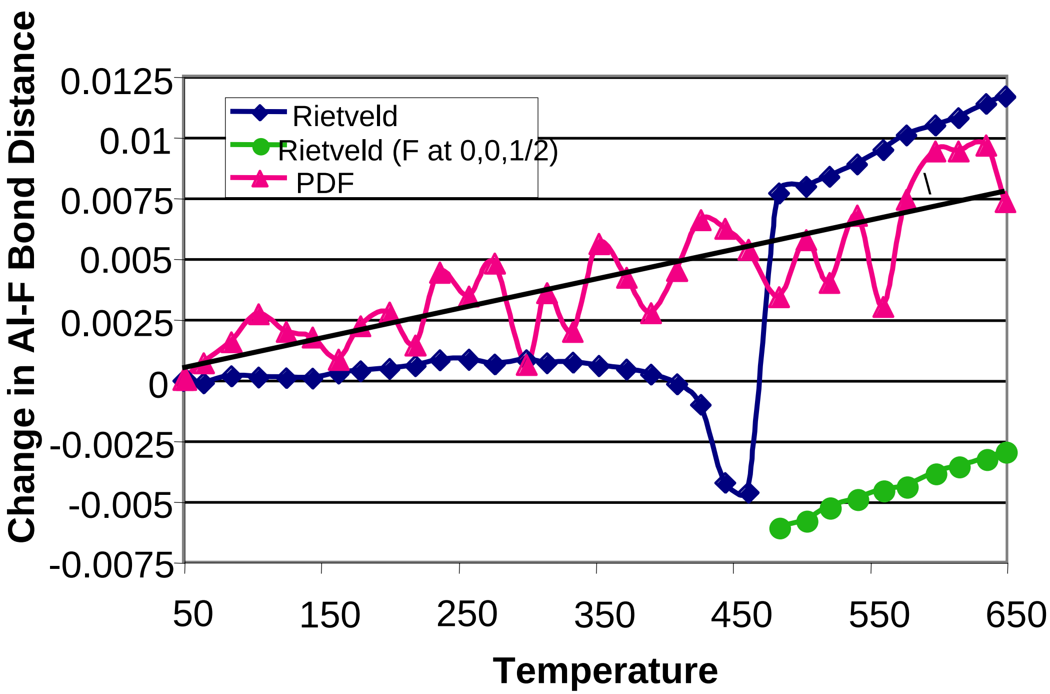
R_{PDF} = 18.60 %

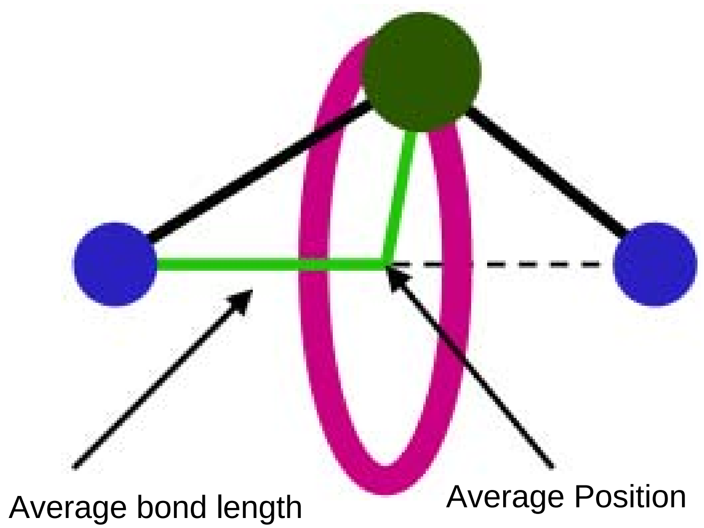


Evidence for Motion of Rigid AlF_6 Octahedra

The experimental results are indicative of a dynamic model where the octahedra are rigid.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

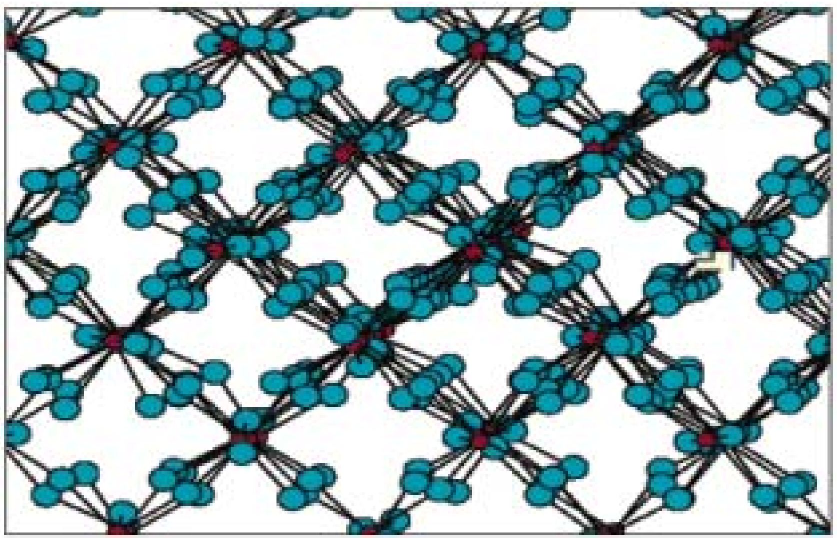




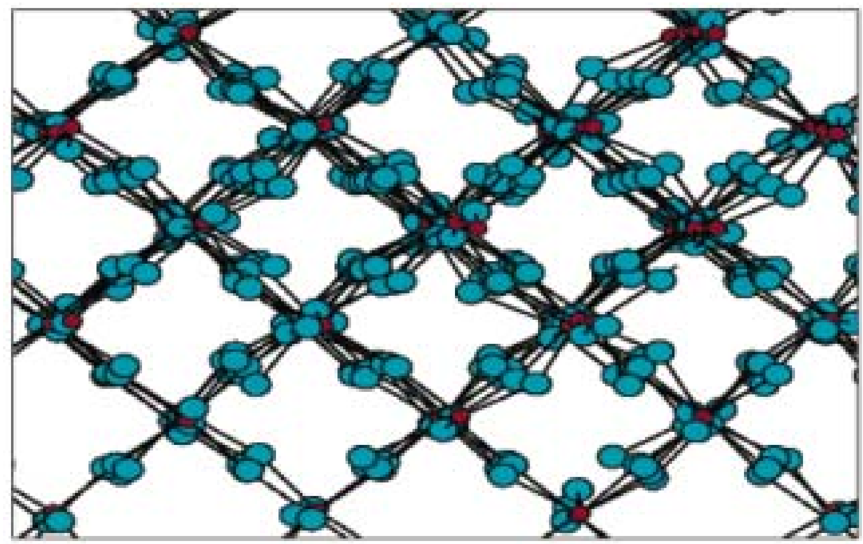
Snapshots from the Molecular Dynamics Simulations

•Molecular Dynamics simulations (Santanu Chaudhuri, Mark Wilson, Paul Madden)

•MD is ideally suited for comparison with total scattering methods.



500 K (Rhom)



900 K Cubic

Chaudhuri, Chupas, Wilson, Madden, Grey *Journal of Physical Chemistry* 108 (2004) 3437.

Snapshots from the MD

•Molecular Dynamics simulations (Santanu Chaudhuri, Mark Wilson, Paul Madden)

Chaudhuri, Chupas, Wilson, Madden, Grey *Journal of Physical Chemistry* 108 (2004) 3437.

Partial Radial Distribution Functions from MD

Al-F

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Al-Al

MD allows the determination of partial pair correlations

- The Al-F bond distance does not show significant changes as a function of temperature
- However, broadening of the Al-F correlation is clearly observed.
- The Al-Al gradually increase as a function of temperature

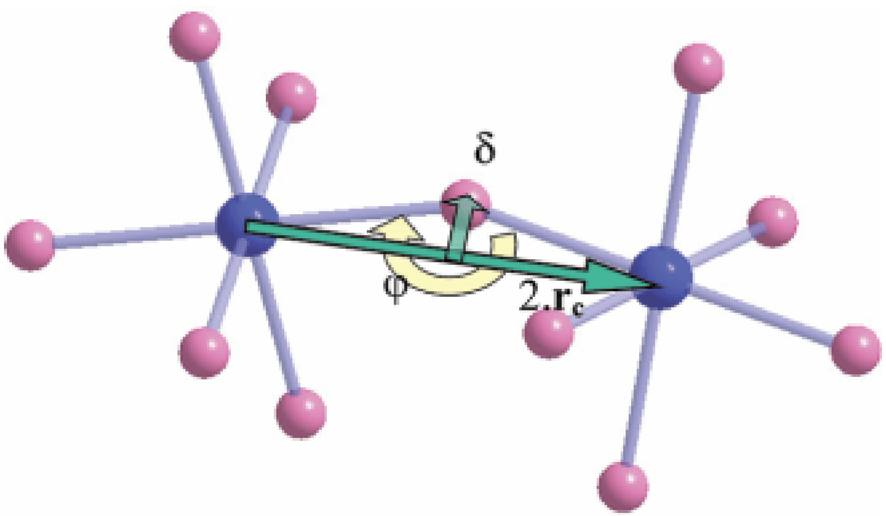
Correlation Functions from MD

$\mathbf{r}_c = (\mathbf{r}_k - \mathbf{r}_l)/2 + \mathbf{r}_l$

$\delta = \mathbf{r}_i - \mathbf{r}_c$

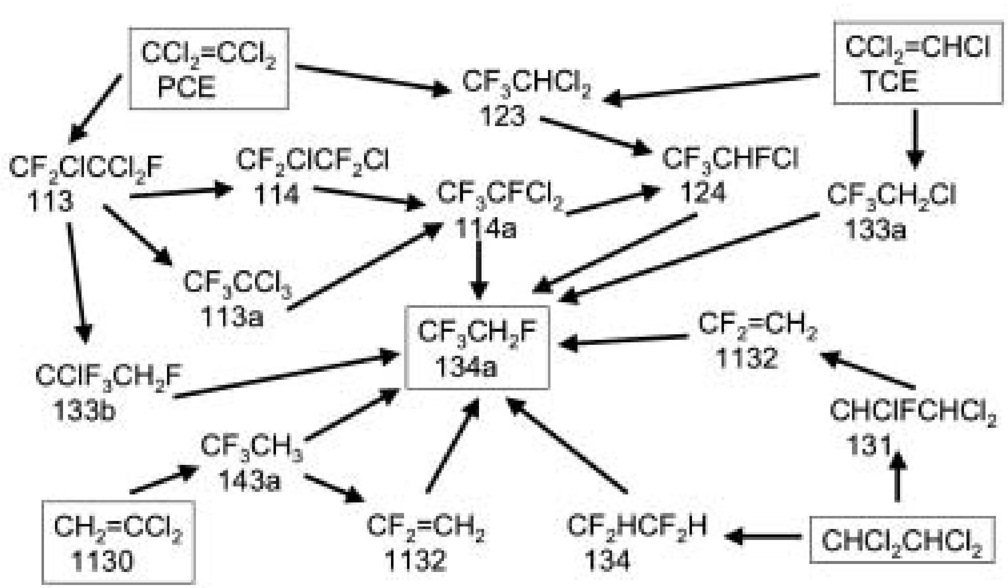
$C_{disp}(t) = \langle \left| \delta_i(t) \right| \left| \delta_i(0) \right| \rangle$

$C_{angle}(t) = \langle \left| \hat{\delta}_i(t) \bullet \hat{\delta}_i(0) \right| \rangle$

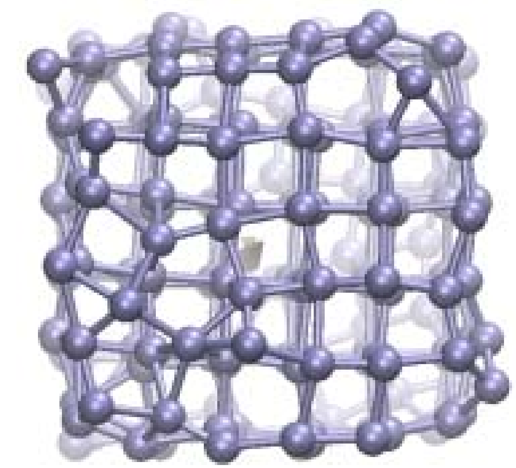


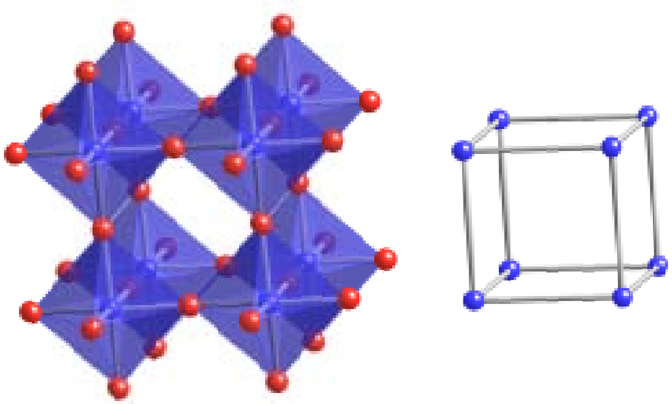
QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

AlF_3: An example of an Industrial Important Heterogeneous Catalyst

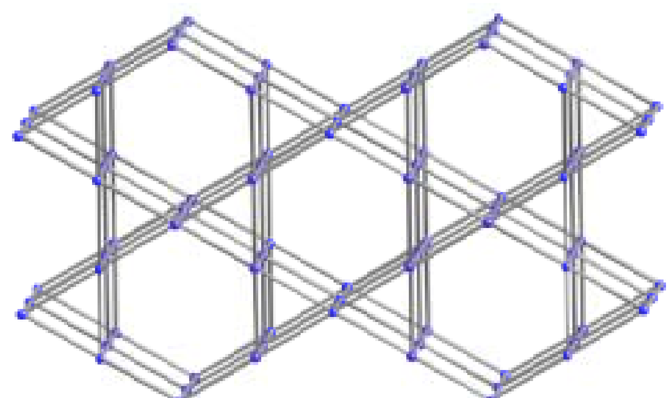


nano-AlF_3 from PDF and MD





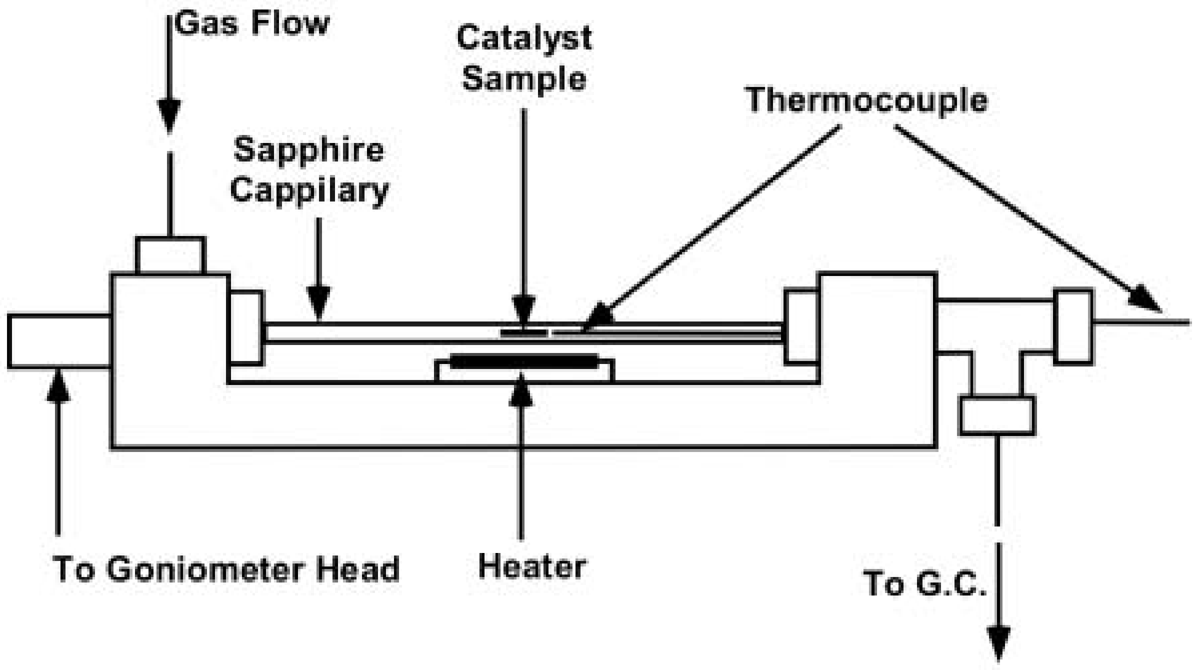
Catalytically inactive α-AlF_3



Catalytically inactive β-AlF_3

Studying Local Structure During Chemical Reactions

Utilize a reaction cell designed to accurately control temperature and control the flow of gases over a sample.



Ceria as a Catalyst

Ceria is a major component of “Three Way” Catalysts: Which Simultaneously treat the reducing pollutants CO and C_xH_y, and the oxidizing pollutant NO_x

Oxidation: $2\ CO + O_2 \rightarrow CO_2$

$C_xH_y + O_2 \rightarrow CO_2 + H_2O$

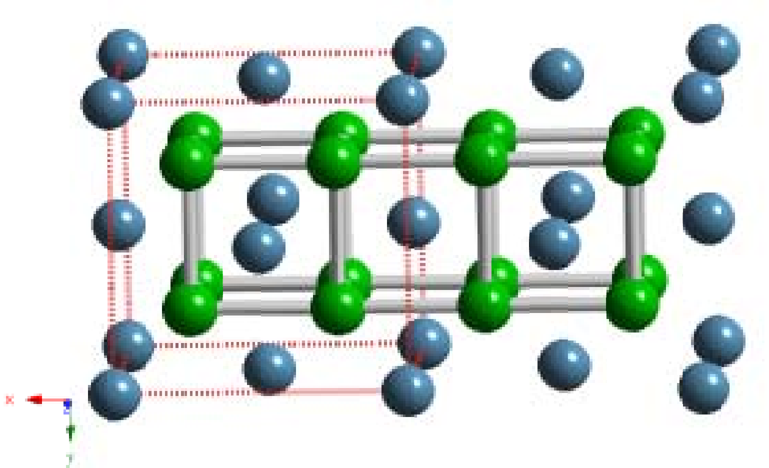
Reduction $2\ CO + 2\ NO \rightarrow 2CO_2 + N_2$

$C_xH_y + NO \rightarrow CO_2 + H_2O + N_2$

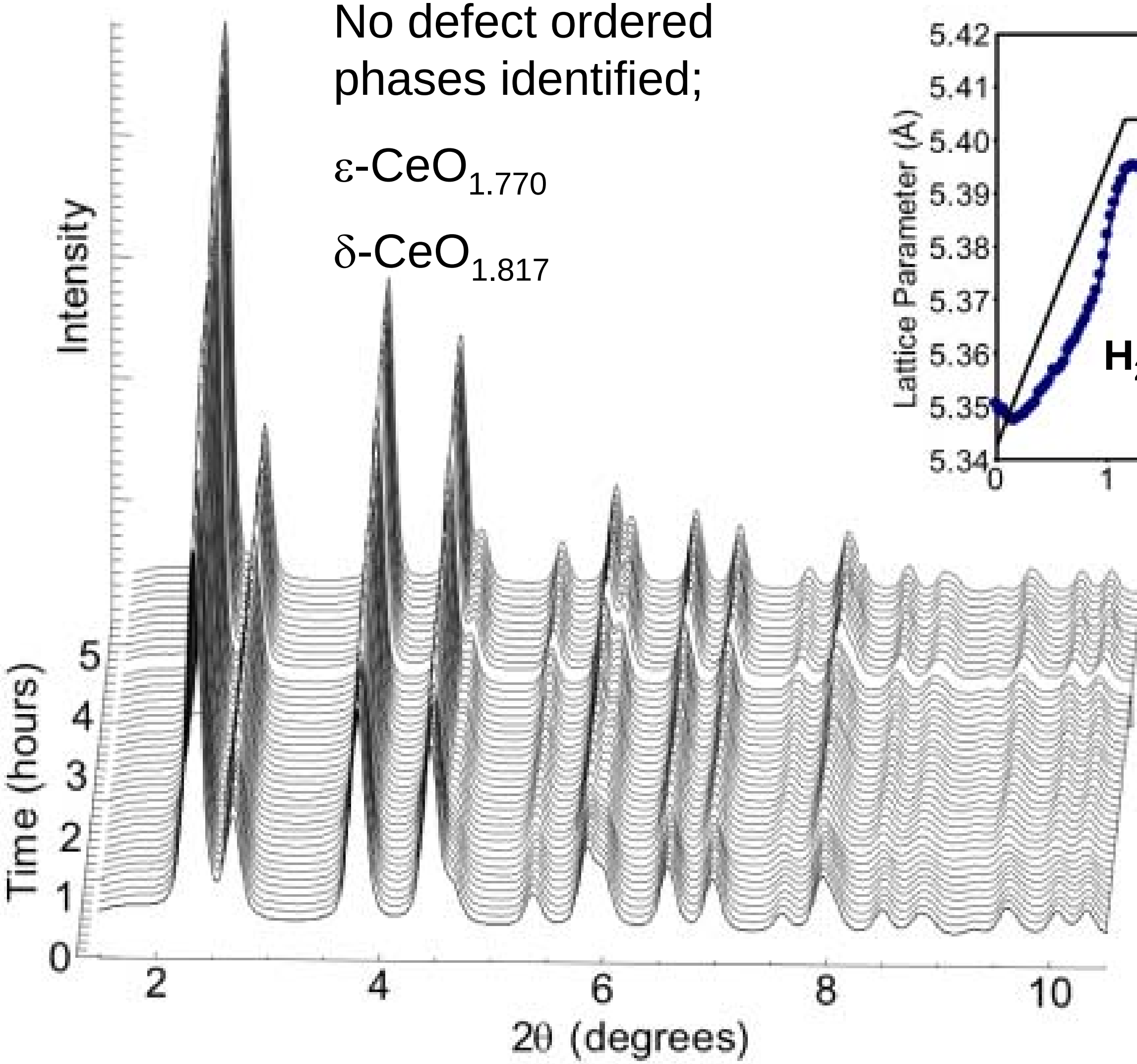
Ceria acts as an oxygen reservoir to stabilize the air/fuel ratio

Fluorite structure with variable composition

CeO_x $1.75<x<2.0$



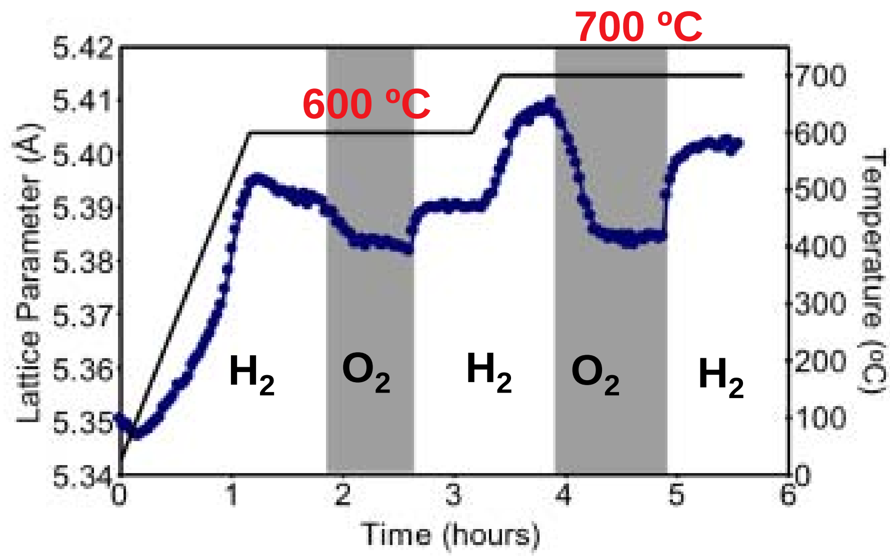
In-situ Reduction of Ceria



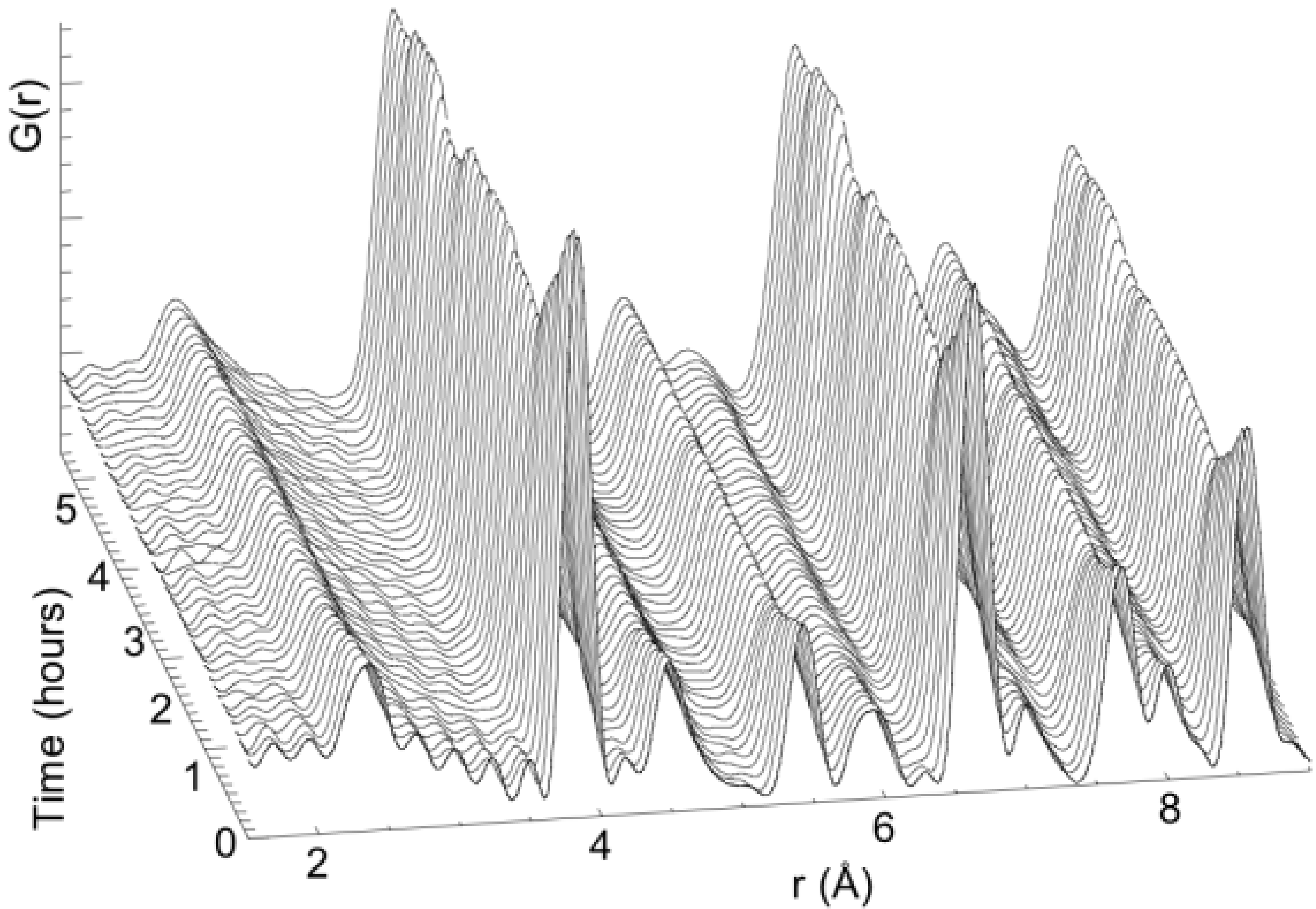
No defect ordered phases identified;

ε-$CeO_{1.770}$

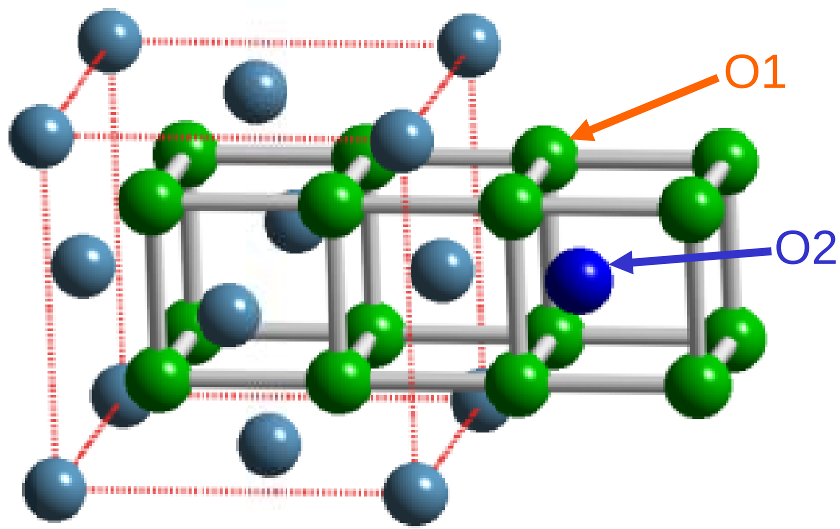
δ-$CeO_{1.817}$

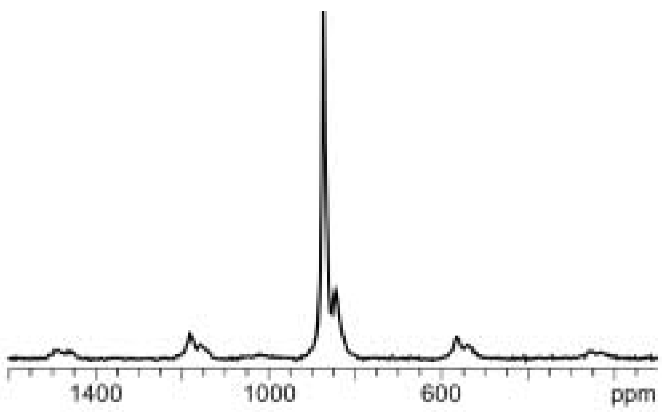


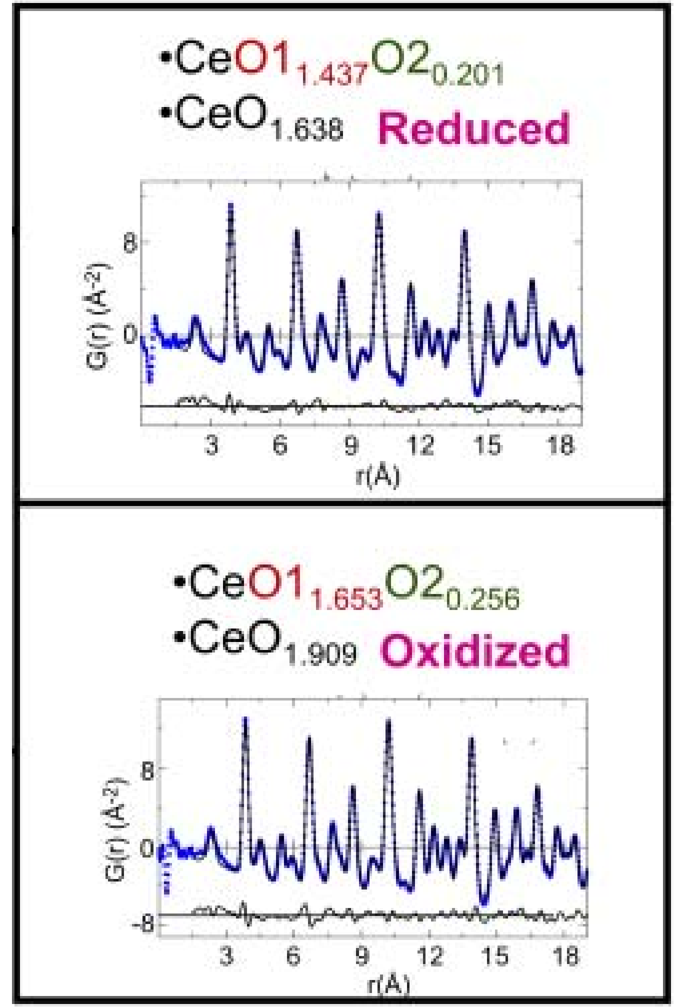
Studying Local Structure During Chemical Reactions



Frenkel Defects in nano-CeO_2



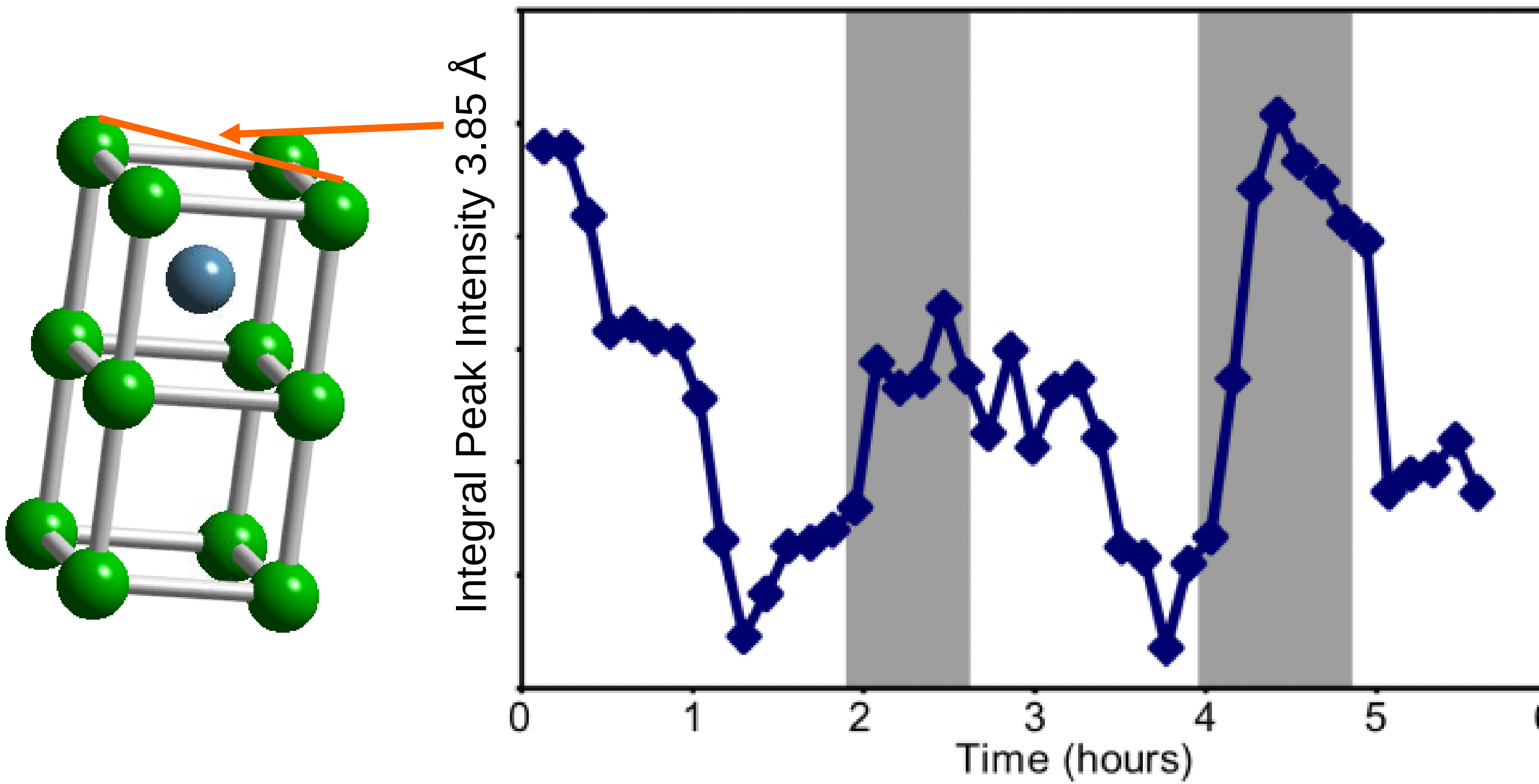




Mamontov and Egami *Journal of Physics and Chemistry of Solids* 61 (2000) 1345.

Nano-CeO_2: Changing Oxygen Content

Oxygen is removed from the 01 site in nano-Ceria on Reduction



Faster Area Detectors

For PDF measurements we need to be able to average of a large solid angle to obtain adequate counting statistics.

Faster Readout: 7-30 Hz

Image Plate ~1min.

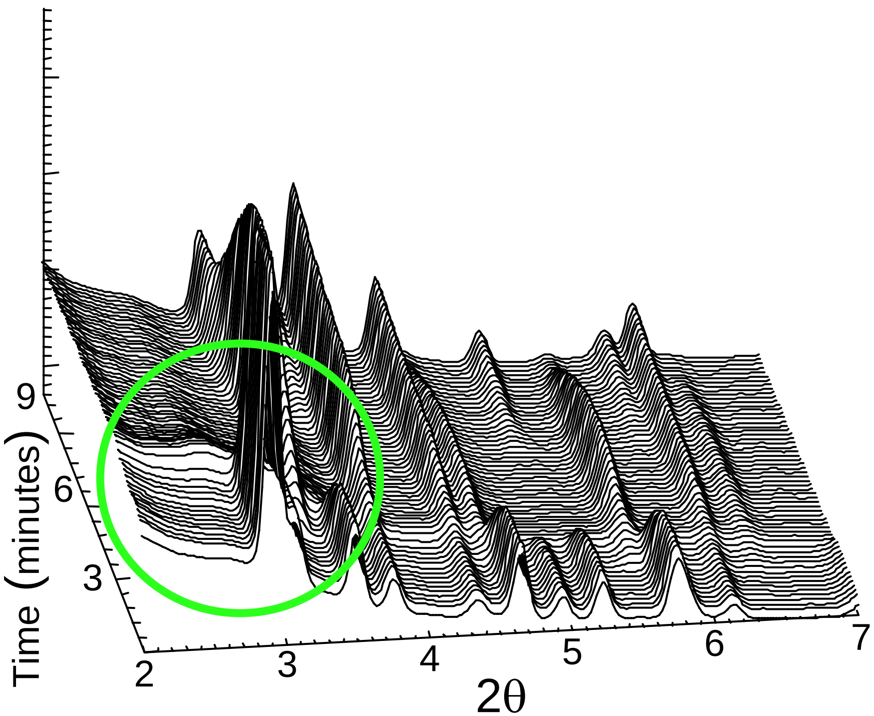
CCD ~ 4 sec.

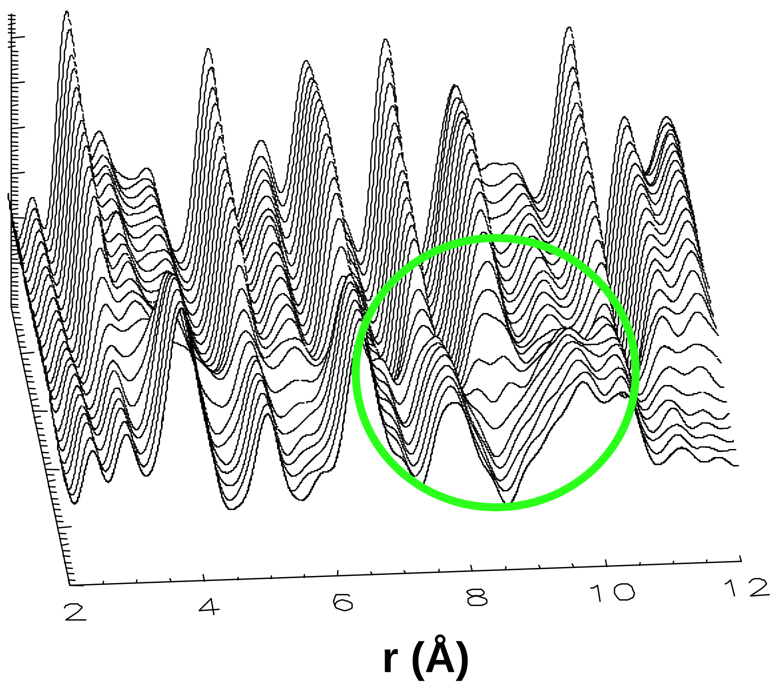
Studying Local Structure During Chemical Reactions

•Potential Hydrogen Storage Material

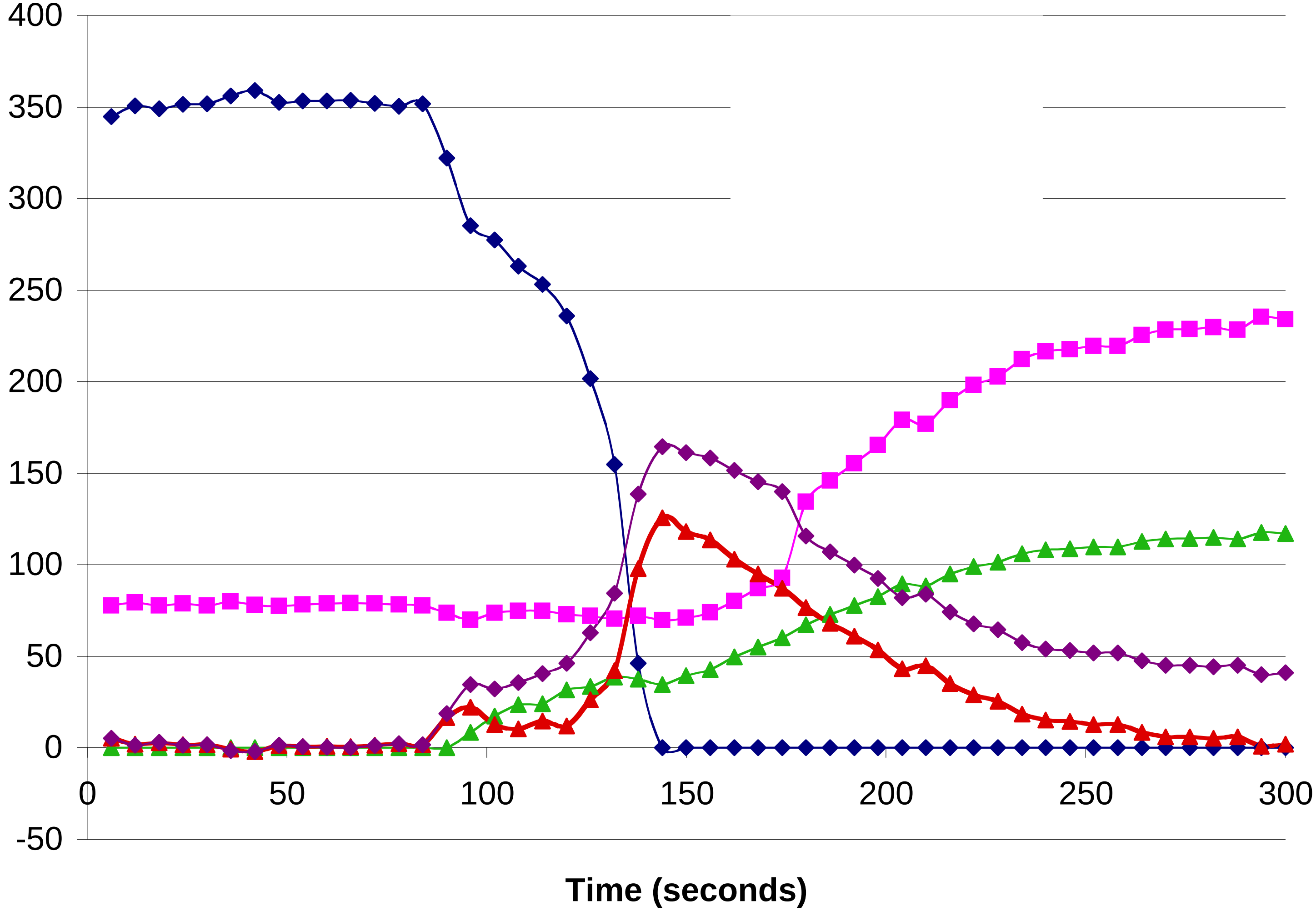
$NaAlH_4 \rightarrow 2/3\ Al + 1/3\ Na_3AlH_6 + H_2 \rightarrow NaH + Al + 3/2\ H_2$

Diffraction experiments with 1 second resolution necessary to isolate amorphous phase





Studying Local Structure During Chemical Reactions



Final Thoughts

•The simple conclusion: In-situ experiments are critical to correlate structure/property relationships.

What is needed to improve and expand the application of in-situ studies?

Instrumentation

High Energy X-rays, Detectors

Advances in Modeling

Incorporating advances in modeling techniques

Ancillary Equipment

Optimized control of the sample environment

Acknowledgements

•Clare Grey	SUNY-Stony Brook
•Santanu Chaudhuri	SUNY-Stony Brook (currently BNL)
•Paul Madden	Oxford University
•Mark Wilson	University College London
•Jon Hanson	Brookhaven National Laboratory
•Peter Lee	APS, Argonne National Laboratory
•Sarvjit Shastri	APS, Argonne National Laboratory
•Yan Gao	General Electric
•Kenneth Kump	General Electric
•German Vera	General Electric
•C. Shawn Rogers	General Electric
•Simon Billinge	Michigan State University
•Xiangyun Qiu	Michigan State University

•*Work supported by Department of Energy, Office of Basic Energy Sciences. Work at the APS was supported by U.S. Department of Energy, Office of Science under contract W-31-109-ENG-38*